THE CRYSTAL STRUCTURES OF THREE NEW VANADIUM OXIDE MINERALS

By Howard T. Evans, Jr., and Mary E. Mrose

Trace Elements Investigations Report 684

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ABSTRACT

Three new vanadium oxide minerals from sandstone deposits have been characterized by the techniques of X-ray diffraction and crystal structure analysis. Häggite, $V_2O_3 \cdot V_2O_4 \cdot 3H_2O$, from Carlile, Wyo., occurs as small black crystals intergrown on a fine scale with a second incompletely described vanadium oxide phase. Doloresite, $3V_2O_4 \cdot 4H_2O$, occurs commonly on the Colorado Plateau in dark brown crystalline masses as an alteration product of montroseite. Duttonite, $V_2O_4 \cdot 2H_2O$, is found as pale brown crystals coating cavity walls at the Peanut mine, Montrose County, Colo. All three have monoclinic crystal structures based on single and double VO_6 octahedron chains linked into various types of sheets.

INTRODUCTION

The vanadium-uranium ores of the Colorado Plateau are characterized by the prevalence of a number of low-valence vanadium oxide minerals, usually occurring as fine-grained mixtures. Extensive mineralogical studies have been fruitful in elucidating the mineral suite (Weeks and Thompson, 1954), but the exact nature of the oxide phases present has been learned mainly through X-ray diffraction and crystal structure study. Thus, the primary vanadium oxide mineral montroseite, VO(OH), was first identified (Evans and Block, 1953), and the mechanism of its oxidation under weathering conditions ascertained (Evans and Mrose, 1955), by crystal structure studies. In the meantime, several new oxide minerals have been discovered in a continuation of these studies. Three of these are briefly described herewith.

HÄGGITE

Häggite, named in honor of Gunnar Hägg of the University of Uppsala, Sweden, is a black oxide with the composition $V_2O_3 \cdot V_2O_4 \cdot 3H_2O$, identified by structure study of crystals separated from a sandstone drill core from Carlile, Wyo. These crystals give double patterns indicating the presence of two oxide phases intergrown on a fine scale in parallel orientation. One, designated phase A, is identified as häggite; the other, phase B, is closely related to doloresite, which is described below. Since chemical analysis was clearly unfeasible, it was necessary to determine the chemical nature of häggite directly by crystal structure analysis. The monoclinic unit-cell volume is 173.9 A^3 which will accommodate 10 oxygen atoms of specific volume 17.4 A^3. The Patterson synthesis made from the intensities of the ($\underline{h}0\underline{\ell}$) reflections showed the presence of zigzag VO_6 octahedral chains similar to those found in montroseite (Evans and Block, 1953). A satisfactory agreement of observed and calculated intensities was obtained for a structure in which these chains are joined laterally into sheets, as shown in figure 1a. The crystallographic data and preliminary atomic position parameters, which give a reliability factor of 0.16, are as follows:

Symmetry: monoclinic, space group $\underline{C}2/\underline{m}$ ($\underline{C}_{2\underline{h}}^{3}$)

Unit cell: $\underline{a} = 12.17 \pm 0.05$ A

$\underline{b} = 2.99 \pm 0.01$

$\underline{c} = 4.83 \pm 0.02$

$\beta = 98^\circ 15' \pm 5'$

Cell content: $H_6V_4O_{10}$

Parameters:	$\underline{x}$	$\underline{z}$
4V in ($\underline{i}$)	0.138	0.396
$2O_1$ in ($\underline{c}$)	0	$\frac{1}{2}$
$4O_2$ in ($\underline{i}$)	0.107	0.146
$4O_3$ in ($\underline{i}$)	0.307	0.324

This structure leads to a unit-cell content of $H_{\underline{n}}V_4O_{10}$. The hydrogen atoms can be located indirectly by the measurement of bond lengths. The $V\text{-}O_1$ distance is short, 1.82 A, indicating that the valency of O_1 is saturated and has no hydrogen associated with it. Six short interlayer O-O distances, four of 2.68 A and two of 2.69 A, indicate the presence of 6 hydrogen bonds in the unit cell, tying the sheets together. The cell content therefore has $\underline{n} = 6$ and the formula may be written $V_2O_3 \cdot V_2O_4 \cdot 3H_2O$, or $V_2O_2(OH)_3$.

DOLORESITE

Doloresite (Stern, Stieff, Evans, and Sherwood, in press), which has the composition $3V_2O_4 \cdot 4H_2O$, is a common mineral on the Colorado Plateau. It is almost always intermixed with paramontroseite, from which it is apparently formed under weathering conditions. The crystallography of doloresite was a puzzle until it was found that it could be explained in terms of the unit cell measured for phase B of the oxide from Carlile, Wyo. This cell is monoclinic, but because of imminent submicroscopic lamellar twinning on (100), the single-crystal patterns of doloresite have a body-centered orthorhombic appearance. The structure of the Carlile phase B was readily determined from Patterson syntheses of the $(h0\ell)$ intensities, and is shown in figure 1b. The structure is similar to that of häggite, except that the double octahedral chains alternate with single octahedral chains in the sheets. The structure factors for this arrangement give a reliability factor of 0.22 for intensities measured on doloresite from Monument Valley, Ariz. The crystallographic data and parameters are as follows:

Symmetry: monoclinic, space group $C2/m$ (C_{2h}^3)

Unit cell: $a = 19.64 \pm 0.06$ A

$b = 2.99 \pm 0.01$

$c = 4.83 \pm 0.02$

$\beta = 103°55' \pm 5'$

Cell content: $H_8V_6O_{16}$

Parameters (tentative):

	x	z
$2V_1$ in (c)	0	$\frac{1}{2}$
$4V_2$ in (i)	0.172	0.369
$4O_1$ in (i)	0.014	0.738
$4O_2$ in (i)	0.083	0.468
$4O_3$ in (i)	0.171	0.064
$4O_4$ in (i)	0.195	0.719

The unit-cell content is $H_{\underline{m}}V_6O_{16}$. By structural arguments similar to those applied to häggite, m cannot be greater than 10. Chemical analysis of the best purified doloresite shows that trivalent vanadium is not present in significant amounts, indicating that m should be 8. The formula may therefore be written $3V_2O_4 \cdot 4H_2O$, or $V_3O_4(OH)_4$. It is still uncertain whether the Carlile phase B has m = 10, or is identical with doloresite with m = 8. It is hoped that detailed refinement of the structures may provide a definite answer to this question.

DUTTONITE

Duttonite (Thompson, Roach, and Meyrowitz, 1956) has the composition $V_2O_4 \cdot 2H_2O$, and is common at the Peanut mine, Montrose County, Colo. The pale brown transparent crystals are monoclinic but show only a slight distortion from a body-centered pseudo-orthorhombic symmetry. A structure was readily determined which is based on single VO_6 octahedral chains, joined into sheets parallel to (100) by sharing vertices (fig. 1c). The crystallographic data and parameters--which give for the (hk0) reflections a reliability factor of 0.10--based on the pseudo-space group Imcm, are as follows:

Symmetry: monoclinic, space group *I2/c* (C_{2h}^{6})

Unit cell: a = 8.80 ± 0.03 A

b = 3.95 ± 0.02

c = 5.96 ± 0.02

β = 90°40' ± 5'

Cell content: $H_8V_4O_{12}$

Parameters (in *Imcm*, D_{2h}^{28}):

	x	y
4V in (*e*)	0	0.336
$4O_1$ in (*e*)	0	0.754
$8O_2$ in (*g*)	0.100	$\frac{1}{4}$

In this structure, the vanadium atoms are strongly displaced from the centers of the octahedra producing a short V-O distance of 1.65 A. This feature apparently corresponds to the vanadyl ion VO^{+2}, which is known to exist in aqueous solution. These polarized groups are arranged in alternate directions along the octahedral chain, thus doubling the normal chain axis repeat unit of 3.0 A along the *c* axis. The oxygen atoms O_2 are hydroxyl groups which are hydrogen bonded into zigzag chains running along the *b* axis. The polarity of these chains, when ordered, causes the symmetry to be monoclinic, pseudo-orthorhombic; when the polarity is disordered, as in synthetic preparations, the true symmetry is orthorhombic.

Detailed descriptions of the crystal structure studies of these and other oxide mineral phases and the crystal chemical relationships among them will be published at a later date.

This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

REFERENCES

Evans, H. T., Jr., and Block, S., 1953, The crystal structure of montroseite, a vanadium member of the diaspore group: Am. Mineralogist, v. 38, p. 1242-1250.

Evans, H. T., Jr., and Mrose, M. E., 1955, A crystal chemical study of montroseite and paramontroseite: Am. Mineralogist, v. 40, p. 861-875.

Stern, T. W., Stieff, L. R., Evans, H. T., Jr., and Sherwood, A. M., in press, Doloresite, a new vanadium oxide mineral from the Colorado Plateau: Am. Mineralogist.

Thompson, M. E., Roach, C. H., and Meyrowitz, R., 1956, Duttonite, a new vanadium mineral from Peanut mine, Montrose County, Colorado: Science, v. 123, p. 990.

Weeks, A. D., and Thompson, M. E., 1954, Identification and occurrence of uranium and vanadium minerals from the Colorado Plateaus: U. S. Geol. Survey Bull. 1009-B, p. 13-62.

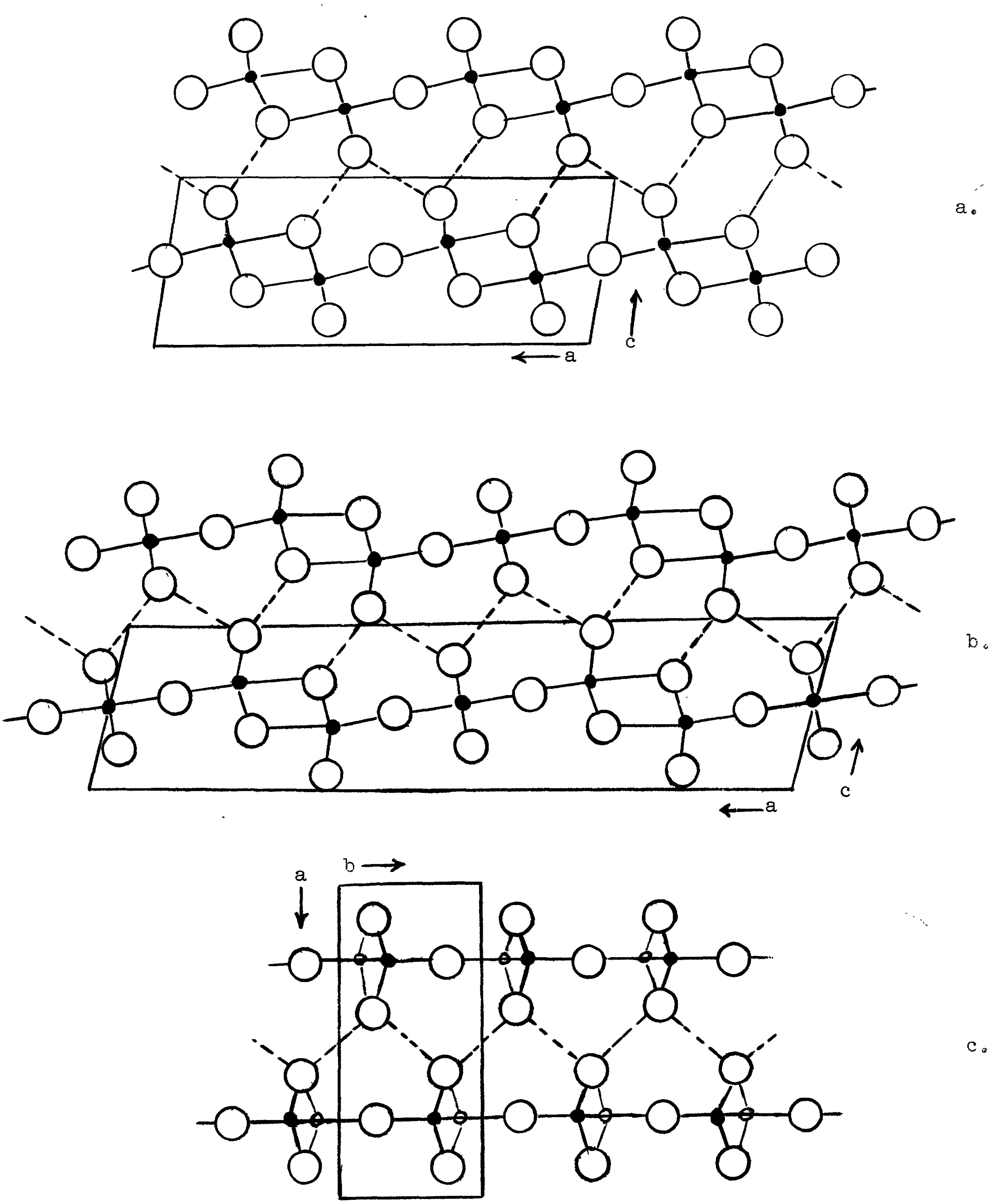

Figure 1.--Crystal structures of (a) häggite, (b) doloresite, and (c) duttonite, viewed along the octahedral chain axes. Dotted lines represent hydrogen bonds.